

Carbon Dioxide Separation from Flue Gas By Phase Enhanced Absorption

(2004.7 – 2007.6)

Annual Report

Reporting Period Start Date: 7/1/2005

Reporting Period End Date: 6/30/2006

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October 2006

DOE Awarding Number: DE-FG26-04NT42128

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ABSTRACT

A new process, phase enhanced absorption, was invented. The method is carried out in an absorber, where a liquid carrier (aqueous solution), an organic mixture (or organic compound), and a gas mixture containing a gas to be absorbed are introduced from an inlet. Since the organic mixture is immiscible or at least partially immiscible with the liquid carrier, the organic mixture forms a layer or small parcels between the liquid carrier and the gas mixture. The organic mixture in the absorber improves mass transfer efficiency of the system and increases the absorption rate of the gas. The organic mixture serves as a transportation media. The gas is finally accumulated in the liquid carrier as in a conventional gas-liquid absorption system.

The presence of the organic layer do not hinder the regeneration of the liquid carrier or recovery of the gas because the organic layer is removed by a settler after the absorption process is completed. In another aspect, the system exhibited increased gas-liquid separation efficiency, thereby reducing the costs of operation and maintenance.

Our study focused on the search of the organic layer or transportation layer to enhance the absorption rate of carbon dioxide. The following systems were studied, (1) CO₂-water system and CO₂-water-organic layer system; (2) CO₂-Potassium Carbonate aqueous solution system and CO₂-Potassium Carbonate aqueous solution-organic layer system. CO₂-water and CO₂-Potassium Carbonate systems are the traditional gas-liquid absorption processes. The CO₂-water-organic layer and CO₂-Potassium Carbonate-organic layer systems are the novel absorption processes, phase enhanced absorption. As we mentioned early, organic layer (transportation layer phase) is used for the increase of absorption rate. Our study showed that the absorption rate can be increased by adding the organic layer. However, the enhanced factor is highly depended on the liquid mass transfer coefficient.

Keywords: Absorption, Phase enhanced absorption, Separation

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LIST OF GRAPHICAL MATERIALS

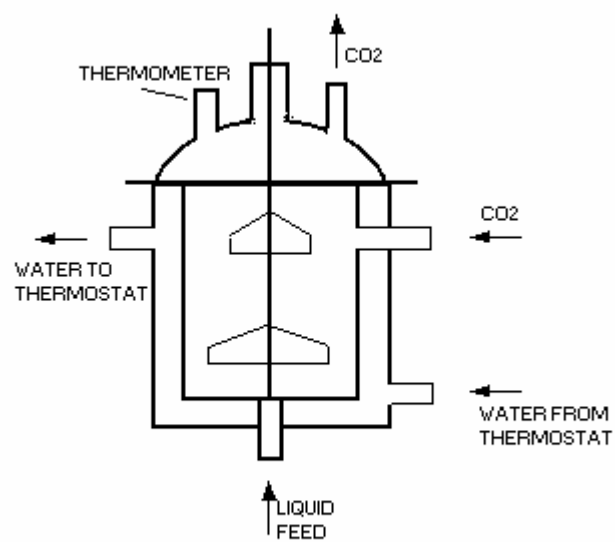


FIGURE 1 STIRRING CELL

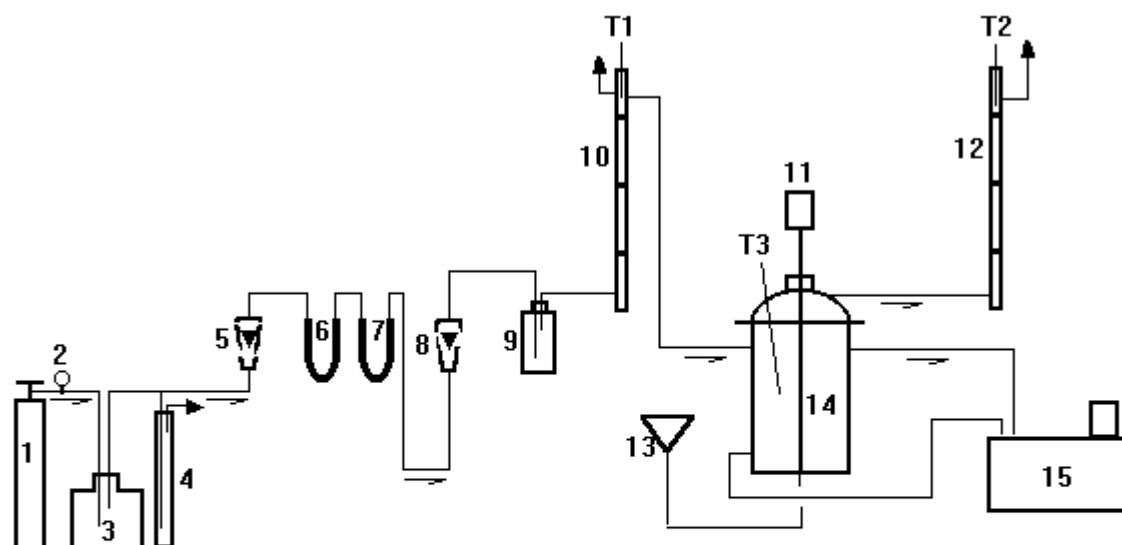


FIGURE 2 EXPERIMENTAL APPARATUS

1 - CO₂ CYLINDER; 2 - REGULATOR; 3 - BUFFER BOTTLE; 4 - PRESSURE STABLE TUBE;
 5, 8 - ROTATING FLOW METER; 6 - SILICON GEL U TUBE; 7 - ACTIVE CARBON U TUBE;
 9 - SATURATOR; 10, 12 - FOAM FILM FLOW METER; 11 - MOTOR 13 - LIQUID FEED FUNNEL;
 14 - STIRRING CELL; 15 - THERMOSTAT; T1, T2, T3 - THERMOMETER

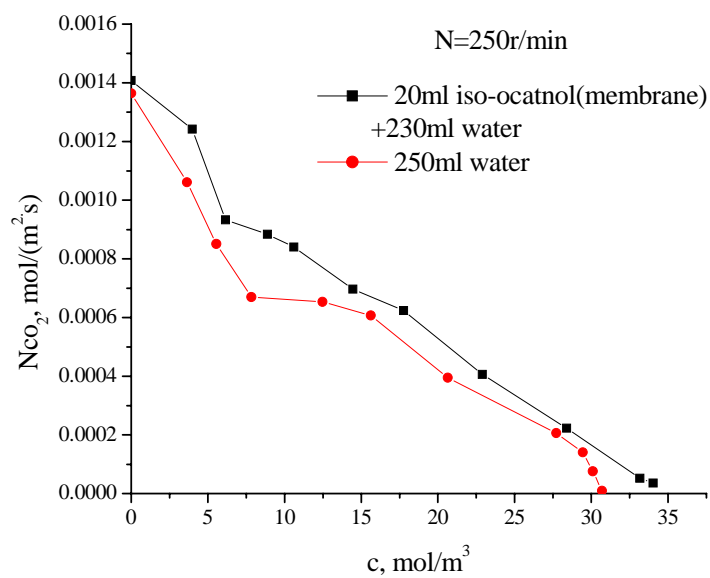


Figure 3. The comparison of CO₂ absorption rate by water(black) and by water with iso-octanol layer(red) at the agitation speed 250 rpm

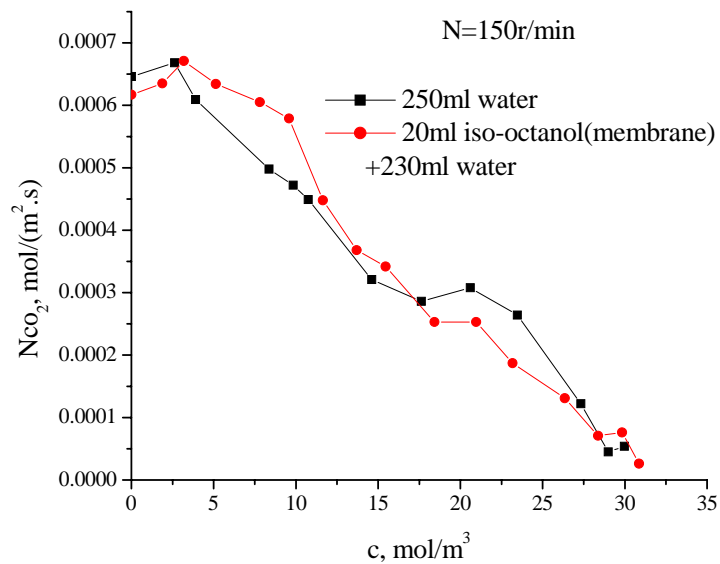


Figure 4. The comparison of CO₂ absorption rate by water(black) and by water with iso-octanol layer(red) at the agitation speed 150 rpm

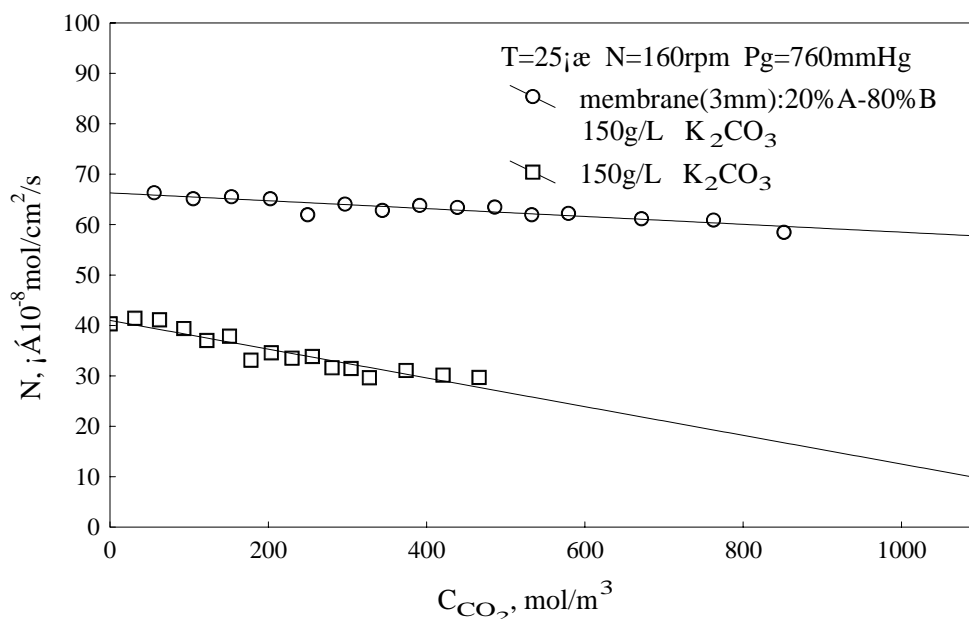


Figure 5. CO₂ absorption rate by 150 g/l K₂CO₃ vs. by Phase Enhanced Absorption (liquid carrier: 150 g/l K₂CO₃; organic layer(3 mm): 20% amine + 80% solvent)

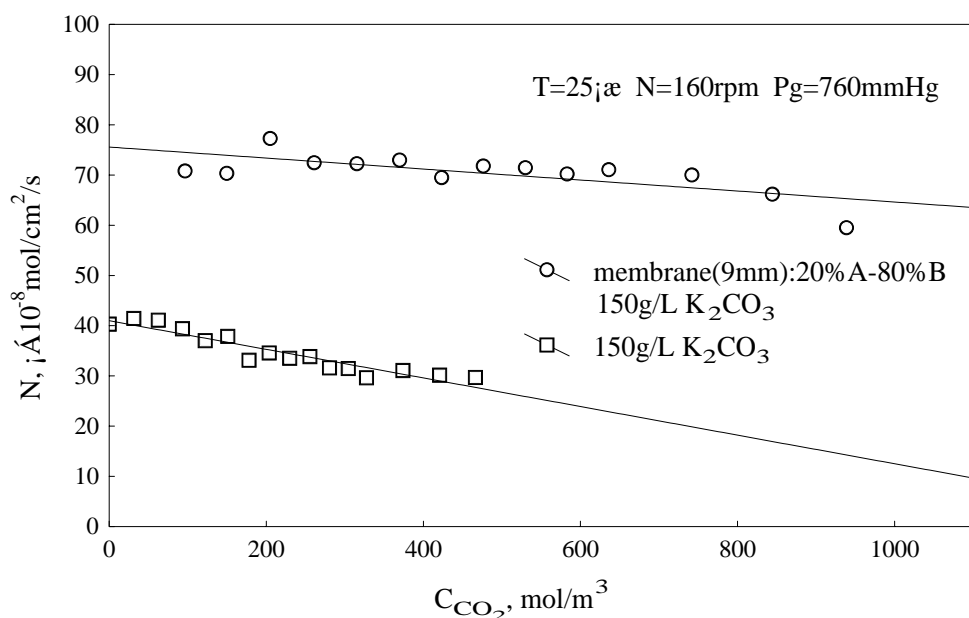


Figure 6. CO₂ absorption rate by 150 g/l K₂CO₃ vs. by Phase Enhanced Absorption (liquid carrier: 150 g/l K₂CO₃; organic layer(9 mm): 20% amine + 80% solvent)

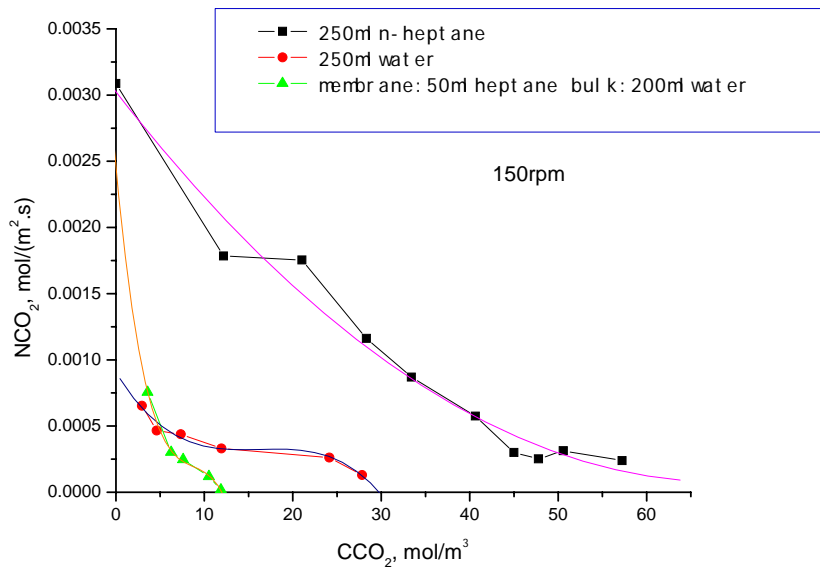


Figure 7. The comparison of CO₂ absorption rates by water, by n-heptane and by water + n-heptane layer at the agitation speed of 150 rpm

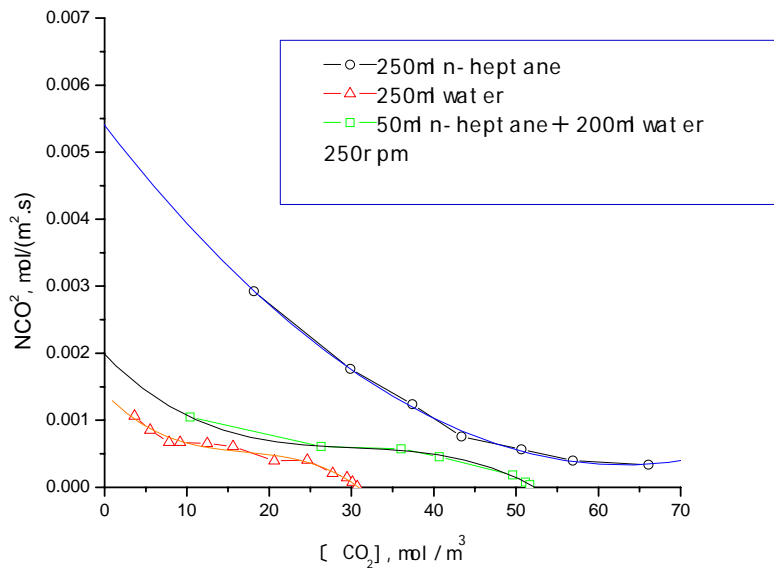
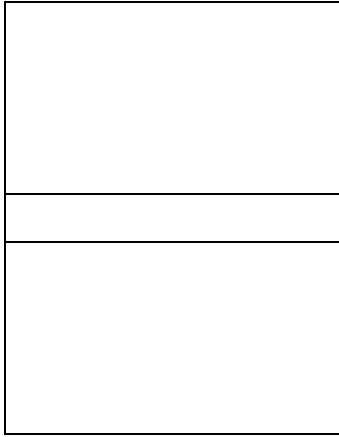
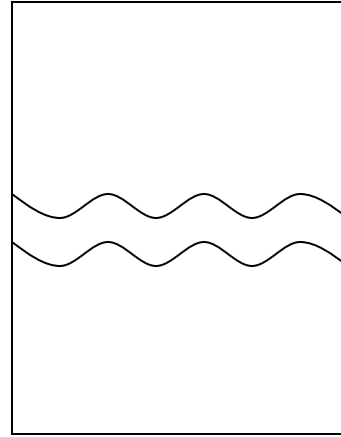


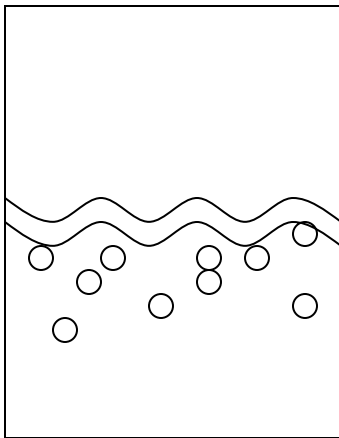
Figure 8. The comparison of CO₂ absorption rates by water, by n-heptane and by water + n-heptane layer at the agitation speed of 150 rpm



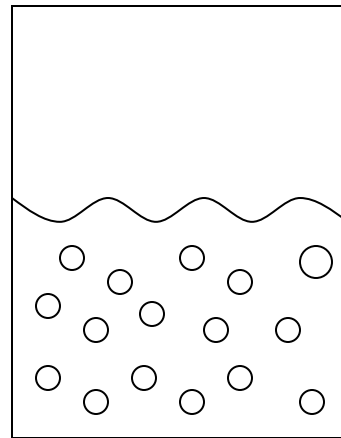
Flow Pattern I



Flow Pattern II



Flow Pattern III



Flow Pattern IV

Figure 9. Liquid flow patterns

INTRODUCTION

Among the methods used to separate and purify gases, the gas-liquid absorption method is one of the most powerful and efficient techniques. A conventional system designed to separate and purify gas consists of a gas phase (mixture of gas including the one to be isolated) and a liquid phase (solution that maximizes absorption).

In chemical absorption, the chemical compounds in the liquid solution react with the gas to form other compounds. This process serves two major purposes. First, chemical reaction with the gas can increase the carrying capacity of the absorbed gas. Second, it can reduce the mass transfer resistance or increase mass transfer coefficient. Both effects contribute to an increased absorption rate. However, such chemical reactions have setbacks: they hinder the release of the absorbed gas from the liquid solution.

Arthur L. Kohl and Fred C. Riesenfeld[1] in their book “Gas Purification,” Gulf Publishing Company (1985) at page 235, discuss the effects of promoters or activators on the carbon dioxide absorption rate and vapor-liquid equilibria. Compared with hot potassium carbonate solutions, diethanolamine (DEA) and sterically hindered amines were found to be very effective in increasing the absorption rate of carbon dioxide. However, the partial pressure of carbon dioxide at equilibrium decreases after an activator is added into the carbonated solution. This means that it is more difficult to recover carbon dioxide from the activated solution than from a solution containing no activator.

Although amine compounds are commonly added into the aqueous solution of alkaline salts in a conventional absorption system, these types of absorbents have

numerous setbacks. They increase the difficulty of carbon dioxide regeneration from the liquid carrier. The method discussed in this report, the phase enhanced absorption, significantly increases the absorption rate of carbon dioxide. At the same time, adding an organic layer to the conventional system does not further hinder regeneration.

Theory

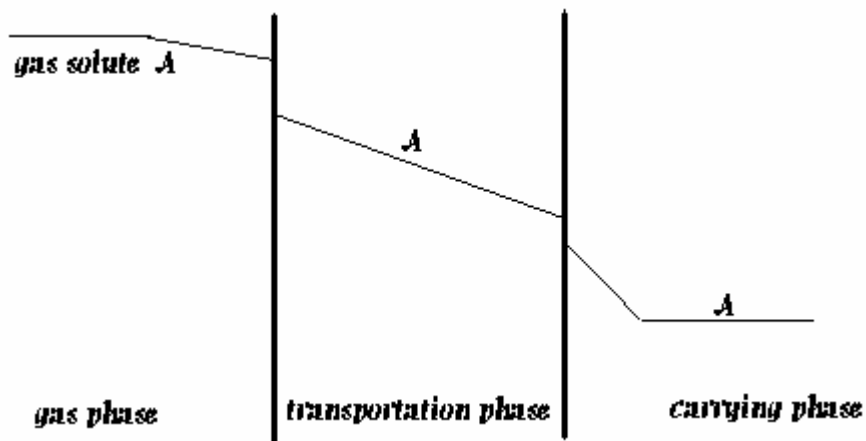
Absorption is a process by which one or more components of a gas mixture are transferred to a liquid where it is soluble. There are two types of absorption: they differ by the nature of the interaction between absorbent and absorbate. In the process of a physical absorption, the gas component being absorbed is simply dissolved in the liquid absorbent. However, the solute does not react chemically with the absorbent. In the case of chemical absorption, there is a chemical reaction between the gas component being absorbed and a component in the liquid to form a compound. In a chemical absorption, the chemical reaction between the gas solute and some component in the liquid solution enhances the absorption rate of the gas.

The phase enhanced absorption features an organic compound in addition to the traditional gas and liquid components. Adding an organic compound or mixture into the absorption system increases the absorption rate of the gas significantly. In phase enhanced absorption, more than one liquid phase is involved in absorbing the gas. One of the liquids serves as an absorbing solution (carrying phase), where the gas is ultimately accumulated. The other liquid, the transportation layer (transportation phase), plays the role of transporting the gas from the gas mixture to the absorbing solution and increasing the absorption rate of the gas. This transportation layer is composed of an organic

compound and simply plays the role of accelerating the transport of the gas to be isolated (in the case carbon dioxide) from the gas phase to the carrying phase.

Due to the added organic layer, phase enhanced absorption has a unique mass transfer model. The gas to be isolated first separates from the bulk of the gas phase and comes in contact with the interface of the transportation phase. This liquid layers absorbs the gas. The absorption is either physical or chemical. In other words, while in the transportation phase, the gas solute may react with the components in transportation phase. In the next step, the gas solute dissolved in the transportation phase passes through the interface between the transportation phase and the carrying phase, and enters into carrying phase. Once the gas is in the carrying phase, the gas solute may exist in two forms: it may be physically dissolved or in a chemical compound resulting from a reaction between the gas and a component of the carrying phase.

The function of the transportation phase is to deliver gas solute from the gas phase to the carrying phase and to increase the absorption rate. Viewed with the film theory, the phase enhanced absorption mass transfer model can be summarized in the following sketch:



MASS TRANSFER MODEL

This report examines the absorption rate of carbon dioxide with phase enhanced absorption and compares this rate to that of a conventional gas-liquid absorption method (without the transportation layer). In our experiments, carbon dioxide gas was ultimately absorbed by water and sodium carbonate aqueous solution(carrying phase). The experiments that follow are designed to demonstrate that adding a liquid phase consisting of an organic compound significantly improves the absorption rate of carbon dioxide.

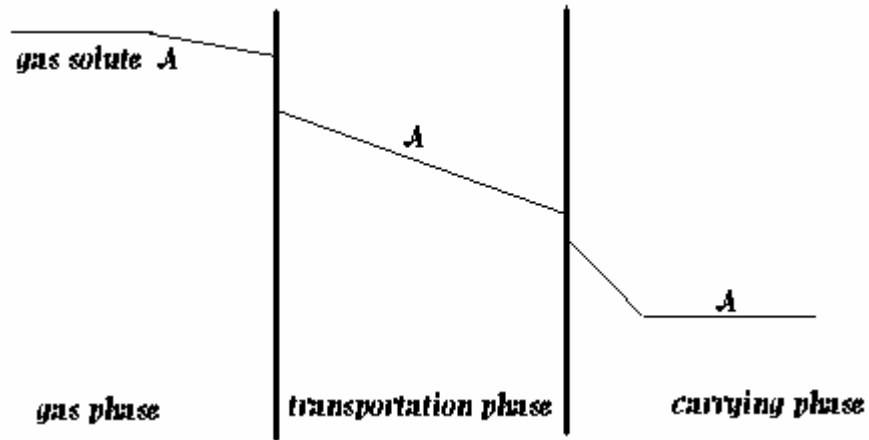
EXECUTIVE SUMMARY

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EXPERIMENTAL

Experimental Method and Apparatus

Apparatus:

Phase enhanced absorption can be demonstrated using a simple system consisting of a stirring cell and a series of connecting apparatuses, all sketched and explained below. Figure 1 is a sketch of a stirring cell, the most important component that includes the three phases unique to the phase enhanced absorption method. The remaining apparatus necessary to measure the absorption rate is sketched in Figure 2. The stirring cell described is also identified in Figure 2.

The stirring cell, made of glass, contains all three phases of a phase enhanced absorption system (gas phase, organic layer, and aqueous solution). The cell's inner diameter is 121 mm and its depth is 130 mm. Two agitating blades, one for the aqueous phase, one for the gas phase, are driven by a direct current motor. The agitating speed is monitored. The rest of the experimental apparatus is shown in Figure 2. The function of each component of the experimental system is explained below.

Method:

To measure the absorption rate of carbon dioxide in the system maintained in the stirring cell, the gas originating from the initial cylinder must pass through the series of apparatus to flow out of the flow meter (12). First, the carbon dioxide cylinder (1) releases carbon dioxide, which passes through the buffer bottle (3) and the pressure stable tube (4). The gas flow rate is controlled and measured by the rotating flow meters (5 and 8). The gas clean system consists of two U tubes. The first U tube (6) is filled with silicon gel and the second U tube (7) is filled with active carbon. The gas is saturated

with moisture by the saturator (9). The solution in the saturator is the same solution that is in the stirring cell (14). Gas flow rate is measured by the foam film flow meters (10 and 12) before and after absorption in the stirring cell (14). The difference between two flow rates is the gas absorption rate. After the measurement, the carbon dioxide gas is released.

The absorption rate of gas, carbon dioxide, at time t was determined by the difference of two flow rates, in and out of stirring cell with two foam film flow meters. As the results of the measurement, the relationship of absorption rate r and elapsed time t would be obtained. Integration of absorption rate with elapsed time, $r \sim t$, the total amount of carbon dioxide absorbed into the liquid phase can be obtained.

Experimental steps:

- (1) Measure the flow rate of gas in and out of the absorption cell at the same time (volume flow rate);
- (2) Measure the temperature of each foam film flow meter **T1** and **T2**;
- (3) Use idea gas equation to calculate the mass flow rates **r1** and **r2** [mol/s];
- (4) Subtract the flow rate of gas in and out of the absorption cell, which is equal to the absorption rate **r**.

Calculation:

The idea gas equation: $PV = nRT$

Divide by time t : $PV/t = RTn/t$

The mass flow rate: $n/t = PV/(tRT)$

Subtract mass flow rate of in and out of absorption cell, which is the absorption rate:

$$r = r_1 - r_2 = (n/t)_1 - (n/t)_2 = PV_1/(tRT_1) - PV_2/(tRT_2)$$

Where t (s) is the elapsed time.

The absorption rate per square area of gas-liquid interface N [mol/(m² · s)]:

$$N = r/\text{area of gas-liquid interface}$$

CO₂ concentration in liquid c:

$$c = \int r \, dt \quad (\text{from } 0 \text{ to } t)$$

RESULTS AND DISCUSSION

1. PHASE ENHANCED ABSORPTION STUDY

1.1 CO₂-water system and CO₂-water-isooctanol system

The CO₂-water system is a traditional absorption process. CO₂ is absorbed into water. This is a physical absorption. The CO₂-water-isooctanol system is a phase enhanced absorption process, where isooctanol forms an organic layer between CO₂ gas and water to increase the CO₂ absorption rate. CO₂ absorption rate by water and by water with isooctanol layer were measured individually under the same experimental condition: the temperature 25 °C, pressure (pure CO₂ gas used): 1 atm, agitation speed: 250 rpm and 150 rpm, and liquid volume: 250 ml. The experimental results are shown in Figures 3 & 4.

Figure 3 is the comparison of CO₂ absorption rate by water and by water + isooctanol layer at the agitation speed 250 rpm. In Figure 3, the line with square indicates the relationship between CO₂ absorption rate by water and CO₂ concentration in liquid. The line with diamond is the relationship between CO₂ absorption rate by water + isooctanol layer and CO₂ concentration in liquid. The liquid was agitated at the speed of 250 rpm

with the total liquid volume of 250 ml(230 ml water and 20 ml isooctanol). As seen in Figure 3, the absorption rate by water + isooctanol layer is higher than that by water.

Figure 4 is the comparison of CO₂ absorption rate by water and by water with isooctanol layer at the agitation speed 150 rpm. In Figure 4, the line with square indicates the relationship between CO₂ absorption rate by water and CO₂ concentration in liquid. The line with diamond is the relationship between CO₂ absorption rate by water + isooctanol layer and CO₂ concentration in liquid. The total volume of the liquid was 250 ml(230 ml water and 20 ml isooctanol). As seen in Figure 4, the absorption rate by water + isooctanol layer is close to the absorption rate by water.

By comparing Figures 3 and Figure 4, the absorption rate by water with isooctanol layer is highly depended on the agitation speed. The reason is that the liquid mass transfer resistance between water and isooctanol layer caused the absorption rate depression at lower agitation speed.

1.2 CO₂-potassium carbonate aqueous solution system and CO₂-potassium carbonate aqueous solution-organic layer system

Using an organic layer to enhance CO₂ absorption rate has been studied. The results are encouraging. Figures 5 and 6 showed that using an organic layer to enhance CO₂ absorption rate. The composition of the organic layer was 20 % activate agent and 80 % other organic solvents. The liquid carrier was potassium carbonate aqueous solution (150 g/l). The experiments were conducted at 25 °C, and 1 atm. 99.99% CO₂ was used in absorption process. Liquid was agitated to provide sufficient mass transfer. The experimental results showed that absorption rates were increased significantly after introducing organic layer into the potassium carbonate aqueous solution. Figure 5 showed

the absorption rate vs. CO₂ concentration in potassium carbonate aqueous solution (885ml) at 3 mm thickness organic layer (40ml). Figure 6 showed the absorption rate vs. CO₂ concentration in potassium carbonate aqueous solution (800ml) at 9 mm thickness organic layer (120ml). Both absorption results of phase enhanced absorption were compared with CO₂ absorption rate by potassium carbonate aqueous solution at the same experimental conditions. As shown in Figures 5 and 6, absorption rates by phase-enhanced absorption are significantly higher than that by traditional absorption.

1.3 CO₂-water system and CO₂-water-n-heptane layer system

Figure 7 is the comparison of CO₂ absorption rates by water, by n-heptane and by water + n-heptane layer at the agitation speed of 150 rpm. CO₂ absorption rate by water + n-heptane layer was the slowest process. CO₂ absorption by n-heptane had the highest rate. While at the agitation speed of 250 rpm (see Figure 8), CO₂ absorption rate by water + n-heptane layer was higher than that by water alone. In both agitation speeds, CO₂ absorption by n-heptane had the highest rate. The experimental results showed that (1) introduction of n-heptane layer into CO₂ – water absorption system is able to enhance the absorption rate by water, however the absorption rate is highly depended on the agitation speed, and (2) because of the higher CO₂ absorption rate by n-heptane or lower mass transfer resistant between the interface of gas and n-heptane, the transportation layer of n-heptane delivers CO₂ from a gas phase into water phase and enhances the absorption rate as long as there is the sufficient mass transfer (agitation) between the two liquid phases is provided.

2. MECHANISM OF PHASE ENHANCED ABSORPTION

To enhance absorption rate, the organic layer introduced into the system should meet the following conditions:

- (1) The mass transfer resistance between organic layer-water is much less than the mass transfer resistance between gas-liquid with the same experimental conditions.
- (2) The mass transfer resistance between the CO₂-organic layer is less than the mass transfer resistance between CO₂-water.
- (3) The sufficient mass transfer from organic layer to water for the dissolved gas, CO₂, is provided.

Conditions (1) and (2) are dependent on the properties of the substances. Condition (3), in our case, is depended on the agitation speed.

Since the absorption rate is highly depended on the agitation speed, and the agitation speed is relative to the liquid flow pattern, the investigation of the liquid flow pattern will disclose the mechanism of the Phase Enhanced Absorption.

Four different flow patterns were observed in our experiments (see Figure 9). In flow pattern I, the organic layer is agitated very gently, the flow in the organic layer is laminar. No convective movement affects the transport of the dissolved gas from gas to water. In this case, the organic layer is the barrier for the transport of dissolved gas into water. Adding the organic layer on the water will decrease the absorption rate for dissolved gas.

With the increase of the agitation speed, the wave on both gas-organic layer interface and organic layer-water interface is observed. This is flow pattern II. In this flow pattern, the convective movement affects the transport of the dissolved gas. In this case, dissolved

gas is transported into water with the aid of convective movement. When the convective movement provides sufficient mass transfer of the dissolved gas, i.e. the transport rate of dissolved gas from organic layer into water is much faster than that from gas into organic layer, adding the organic layer on the water will enhance the absorption rate for dissolved gas.

In flow pattern III (by further increase of agitation speed), part of the organic layer disperses its particles into water. At the same time, the dispersed particles coalesce. The dispersion and coalescence promote the mass transfer of the dissolved gas into water. In flow pattern III, the convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area contribute to the transport of the dissolved gas. In this flow pattern, adding the organic layer on the water will enhance the absorption rate for dissolved gas.

When the agitation speed reaches the highest level, or in flow pattern IV, the organic layer completely disperses its particles into water. In this flow pattern, the organic layer is not a continuous phase. The convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area contribute the transport of the dissolved gas.

In the case of flow pattern III and IV, the dissolved gas is transported into water with the aid of the convective movement, dispersion and coalescence, and the increase of the organic layer-water interface area. The transport rate of dissolved gas from organic layer into water is much faster than that from gas into organic layer. Adding the organic layer on the water will enhance the absorption rate for dissolved gas.

To explain the experimental results, we examine an example of CO₂-water-n-haptane system. Water has slow absorption rate for CO₂ by comparing with organic solvent, n-haptane (see Figures 7 and 8). We know that water and n-haptane are immiscible. In order to increase the absorption rate of CO₂ into water, a layer of n-haptane is added on water. Because of the lower mass transfer resistance between CO₂ and n-haptane, CO₂ dissolved into n-haptane organic layer at a rate 3-4 times faster than that into water (see Figures 7 and 8). At a low agitation speed, 150 rpm, CO₂ absorption rate by water-n-haptane layer was higher than that by water initially. The absorption rate quickly dropped to below the absorption rate by water as the absorption progressed. The initial fast absorption rate was contributed by n-haptane layer. At a low agitation speed, the n-haptane layer was agitated gently. The flow in organic layer was laminar. No convective movement affected the transport of the dissolved gas CO₂. After the n-haptane layer was saturated with CO₂, the absorption rate quickly dropped to below the absorption rate by water. However, at this moment, water contained very little CO₂ (see Figure 7).

When the agitation speed was increased to 250 rpm, CO₂ absorption rate by water- n-haptane layer was higher than that by water all the time (see Figure 8). It was observed that the wave appeared on both CO₂- n-haptane interface and n-haptane-water interface at 250 rpm agitation speed. In this flow pattern, the convective movement affects the transport of dissolved gas CO₂. The dissolved gas CO₂ was transported into water from n-haptane layer with the aid of convective movement. When the convective movement provides sufficient mass transfer of the dissolved gas CO₂, the absorption rate of CO₂ is enhanced.

CONCLUSION

Experiments comparing the absorption rate of a conventional gas-liquid absorption system with that of a modified system using phase enhanced absorption show that phase enhanced absorption exhibits a higher absorption rate.

The new system consists of a gas component (carbon dioxide), an organic layer, and an aqueous solution. The studied systems were as following: (1) CO₂-water system and CO₂-water- isooctanol layer system; (2) CO₂-Potassium Carbonate aqueous solution system and CO₂-Potassium Carbonate aqueous solution-organic layer system; (3) CO₂-water system and CO₂-water-n-haptane layer system. The CO₂-water and CO₂-Potassium Carbonate systems are the traditional gas-liquid absorption processes. The CO₂-water-organic layer and CO₂-Potassium Carbonate-organic layer systems are the novel absorption processes, phase enhanced absorption. As we mentioned early, organic layer (transportation layer phase) is used for the increase of absorption rate. Our study showed that the absorption rate can be increased significantly by adding the organic layer. However, the enhanced factor is highly depended on the liquid mass transfer coefficient. The mechanism is obvious because of the higher CO₂ absorption rate by organic layer or lower mass transfer resistant between the interface of gas and the organic layer, the transportation layer (organic layer) delivers CO₂ from the gas phase into water phase and enhances the absorption rate as long as there is sufficient mass transfer (agitation) between two liquid phases is provided.

Prospects for future progress include the kinetic study, and search for the potential application for CO₂ capture.